Spiral Orbit Tribometry
II. Evaluation of Three Liquid Lubricants in Vacuum

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Abstract

The coefficients of friction and relative degradation rates of three lubricants run in the boundary regime in vacuum are evaluated in a Spiral Orbit Tribometer. This tribometer subjected the lubricants to rolling contact conditions similar to those found in angular contact ball bearings. A multiply alkylated cyclopentane (MAC) hydrocarbon lubricant suffered degradation at a rate almost two orders of magnitude less than the degradation rate of two perfluoropolyalkyether (PFPE) lubricants. l

I Introduction

A new rolling contact tribometer – the Spiral Orbit Tribometer (SOT) – was introduced in the previous paper[1] The SOT is basically a thrust bearing, with one ball and flat races, in which the ball is driven in a spiral orbit by a rotating plate. The force exerted on a “guide plate” that forces the ball back into its initial orbital radius was shown to be related to the coefficient of friction (CoF) of the system. In that paper, termed I, the motions of the ball and the method by which the CoF was obtained were described.

In this paper, we report the results of using the SOT to evaluate the coefficient of friction (CoF) and relative degradation rates of liquid lubricants running in the boundary lubrication regime on steel in vacuum. Significant solid/solid contact in this regime subjects organic molecules trapped in the contact zone to an environment that may be considered chemically aggressive and destructive to the lubricant. The relative degradation rates are determined by employing only μg quantities of lubricant that are consumed or “used up” during a relatively short test. The results are relevant to the operation and longevity of bearings used in mechanisms on spacecraft as well as other mechanisms that operate in vacuum.

II Experimental

Mechanical. The SOT described in I is depicted in Fig.1. For the work described here, it was housed in a stainless steel chamber and evacuated without baking to 1×10^{-8} torr by a turbomolecular pump. A cold cathode ionization gage was used to measure the system pressure. No hot filaments or devices that could inject charge particles into the operating environment and alter organic materials such as lubricants were used during the evaluations described here.

Specimens. All specimens were 52100 bearing steel. This low-chromium steel has a relatively simple microstructure, without the ubiquitous chromium carbides present in steel with higher chromium content, such as 440C steel. The large plates were 2” diameter and the guide plate was .5” diameter. The balls were purchased as Grade 25 bearing balls. The plates were polished to a mirror finish, with 4-7 nm rms roughness measured by optical interferometry. The plates were cleaned by polishing with alumina polishing compound on a soft-clothed polishing wheel, followed by a final rinse with deionized water in an ultrasonicator. Water had a near-zero contact angle on this surface and surface analysis by XPS indicated no impurities other than a small coverage of the usual adventitious carbon. This carbon contaminant coverage was evidently small enough to allow water to spread. The ball was cleaned by rubbing it with chromia polishing compound, followed by the above rinse. Water also spread on its surface and XPS analysis also showed only the same small residual surface carbon.

Lubricants. The three lubricants used in this study are all commercially available. They are designated as 815Z, a linear perfluoropolyalkylether, 143AC, a branched perfluoropolyalkylether (PFPEs), and 2001A, a multiply alkylated cyclopentane (MAC) hydrocarbon. These fluids were unformulated and used as received without further processing. Their vapor pressures were sufficiently low such that no mass loss by evaporation could be measured for the dwell time in vacuum required by these tests (<48 hours).

Lubricant Application. In these tests, lubricant is initially applied only to the ball. Lubricant is transferred to the plates during operation and some can actually be shed to the side of the track, where it is no longer available to be used by the system. To minimize the amount shed and also to minimize the duration of the tests, the smallest possible amount of lubricant, consistent with the ability to measure its mass, was applied to the ball. Lubricant was applied by dripping a dilute solution of the lubricant (~1μg/μL) from a syringe onto a ball spinning on a magnetic chuck and measuring the weight gain after the solvent evaporated. Weight gains of ~20 μg were achieved, with ± 5 μg variability between applications. Although the coverage as deposited was certainly not uniform over the ball's surface, a weight gain of 20 μg corresponds to an *average* film thickness of 21 nm for the PFPEs and 46 nm for the MAC. Possible consequences of non-uniform coverage will be discussed below.

Operating Conditions. The vacuum system pressure during operation was < 2×10^{-8} torr. Pa? The load on the ball was 43 lb, corresponding to a Hertz pressure of 1.5 GPa and a diameter of .4 mm for the region of elastic contact. The ball traced a near-circular spiral 1.8" diameter on the large plates at an orbital rate of 30 rpm, corresponding to a linear speed of ~ 72 mm/sec. It is not possible to form an EHD film that physically separates the ball from the plates under these conditions of high load, low speed and minimal availability of lubricant. The system operates in the regime of boundary lubrication. This was confirmed by a measurement of the electrical resistance through the ball-plate contacts during initial operation. A finding of close to zero resistance indicated appreciable metal-metal contact and the absence of an EHD film. Most of the lubricant molecules are "squeezed out" of the contact and those remaining that actively lubricate are subjected to the severe tribochemical stresses that degrade them. Aside from the initial electrical resistance check, all plates were electrically grounded during the tests. Four tests were run for each lubricant for a total of twelve tests reported here.

III Results

A. Characteristics of a test.

The force profile. Typical "force profiles" – the friction force of the ball sliding on the rotating plate as a function of the ball's position in the scrub[1] – are shown in Fig.2. Two profiles are actually depicted in the figure – one with only the individual data points plotted and another with lines drawn between suppressed data points. The profiles are virtually identical, illustrating the high degree of orbit to orbit reproducibility of the force profile. The profile exhibits small oscillations due to a dynamic "ringing" effect discussed in I. The amplitude of the oscillations ~~are~~ is smaller here than of those in I because the ball orbit speed is less here than it was in I. The friction force is averaged over the indicated interval in the oscillatory region and divided by the load to produce a CoF.

The friction trace. The CoF as a function of orbit number for a typical test is depicted in Fig. 3. The usual term for the plot of CoF as a function of time is "friction trace" and it will be used here. First note that the CoF exhibits some scatter in the first few orbits. This is a characteristic common to all friction traces obtained for these tests and is attributed to the initial non-uniformity of lubricant coverage that is evened out by additional ball orbits. The subsequent orbit to orbit reproducibility of the CoF is illustrated by the inset in Fig. 3, which is an expansion around orbits 56 and 57. The reproducibility is extraordinary, even in this notoriously noisy regime of boundary lubrication. It is conjectured that such reproducibility is due to the continuous exchange of lubricant between ball and plates that results in a sufficiently uniform equilibrium distribution of lubricant on the rolling and sliding surfaces. The CoFs reported below were obtained by averaging 100 values around the 400th orbit of each test. In Fig. 3, the CoF eventually departs from a constant value of .13 and increases rather abruptly, reaching a value of .2 at 1,085 orbits. The test is terminated at CoF=.3. This transition to high friction is common to all the tests reported here. The friction trace has a familiar appearance in that tribological experiments often exhibit such a period of constancy followed by a transition to higher friction that is associated with a failure of lubrication. The nature of this failure in the present case will now be addressed.

Lubricant consumption. The intuitive interpretation of the failure is that it is due to a lack of lubricant on the sliding and rolling surfaces. This interpretation is supported by a post-test examination of the ball and the tracks by infrared microspectroscopy that indicates the *absence* of lubricant that is otherwise easily detectable on specimens not run to failure. The lubricant initially present has been transformed into a non-lubricating state. One such state is that of solid degradation products often denoted as "friction polymer". A micrograph with such material has been shown in Fig. 5 of I. Friction polymer has often been observed and is evidently not effective as a lubricant 2. as is the original lubricant fluid. Another state into which the lubricant is transformed is the gas phase. Volatile fragments of decomposing lubricant can be released into the vacuum chamber and pumped away. Indeed, during tests with the PFPEs, definite pressure increases (~.5x10^{-8} torr) have been observed. Lubricant fragments have also been observed with a residual gas analyzer (RGA). Particularly convincing evidence for lubricant transformation into the gas phase and disappearance of lubricant associated with the failure region of the friction trace is presented in Fig. 4. The figure shows both the intensity, I_{69}, of the m/e=69, CF_3^+ fragment in the RGA and the CoF throughout a test with 143 AC running on 440C steel. There is a background level of I_{69} that immediately increases as rolling commences due to evolution of lubricant fragments. The increase of I_{69} as the system approaches failure is due to the enhanced decomposition rate of the fewer remaining molecules, i.e. increased frictional energy input per remaining lubricant molecule. The rapid decrease of I_{69} in the high friction region is associated with the depletion of lubricant molecules available to be decomposed. The lubricant has been consumed.

Designation of consumption rate. The relative consumption or degradation rate of these lubricants is desired. However, the present approach leads more naturally to expressing the inverse – the lifetime, i.e. the number of orbits to failure, defined as CoF≥.2. The lifetime of the lubricants in these tests will be given in terms of orbits to failure per μg of lubricant initially applied to the ball. These lifetimes will permit the ranking of the robustness or longevity of these lubricants under these test conditions, with the understanding that the degradation rate is related to the inverse of these lifetimes.

B. Test results

The results of the twelve tests – four tests for each of three lubricants – presented in Table 1. A graphical depiction of the lifetimes is presented in Fig. 5. There is a value of CoF and lifetime for each test. No value of CoF or lifetime for a given lubricant falls within the range of values for any other lubricant. Thus a clear distinction between the lubricants run under these conditions can be observed from measurements of CoF and lifetime made here with spiral orbit tribometry.

Discussion

First, it is appropriate to discuss the present approach to lubricant evaluation in terms of the concept of "acceleration". Since evaluation of lubricants in actual service conditions is generally a time-consuming process, completion of tests in shorter times – accelerated tests – have employed higher temperatures, loads or speeds. Such methods may subject the lubricant to conditions that are outside the range found in service and thus raise questions concerning the applicability of the test results. The present approach of limiting the amount of lubricant available to be tested can be regarded as an acceleration technique that does not have these shortcomings.

The reproducibility of the test results is addressed next. The orbit to orbit reproducibility of both the force profile and the CoF obtained from them have been noted above. The CoF's test to test reproducibility is sufficient to permit a clear distinction between the lubricants and thus to allow CoF values to be stated to two decimal places:

815Z: .12   143AC: .13   2001A: .08

Although there is sufficient reproducibility in the lifetimes to distinguish between lubricants, there is definitely more scatter for the lifetime results than for the CoFs. The scatter may be due to (1) inaccuracies in the weight of lubricant actually applied to the ball prior to installation in the apparatus or (2) random differences in shedding of lubricant to the side of the track where it is not available for the back and forth transfer process between ball and track. Although the weight determination may conceivably be improved, the random shedding is an intrinsic characteristic of this apparatus and thus further reduction of scatter in lifetime may not be possible. The scatter in lifetime is, however, small enough to rank the robustness of the lubricants with confidence:

2001A > 143AC > 815Z.

Thus the MAC is clearly more robust under these conditions than either of the two PFPEs. Note, that longer life does not directly correlate with lower CoF since the lifetime of 143AC with CoF=.13 is greater than the lifetime of 815Z with lower CoF=.12.

The results presented here are quantitative for the CoF and are, presumably, of general applicability to those situations where the lubricant operates in the boundary regime. The results for the lifetimes, on the other hand, are specific to this instrument and can only be regarded as semi-quantitative at best. They indicate that under these conditions, the consumption or degradation rate of the MAC is almost two orders of magnitude smaller than that of the PFPEs and that 143AC is a bit more robust than 815Z. It would be desirable to go beyond these semi-quantitative rankings and obtain consumption rates that are of direct applicability to the usual ball bearing configuration. However, this semi-quantitative ranking has, in fact, found experimental confirmation in full scale ball bearing tests reported by Loewenthal et al[2] that found longer life of bearings lubricated with the MAC than with a PFPE.   Jansen et al. ?

The shortcomings of the PFPE fluids as boundary lubricants in vacuum were recognized soon after they were introduced as lubricants in spacecraft mechanisms. The observation of "brown sugar" degradation products prompted a series of studies that have resulted in a scenario[3] for the sequence of events that culminate in the consumption of PFPE. The chemical events start with the mechanical scission or tearing apart of the PFPE chain by the mechanical forces at the ball-plate contact[4,5]. The severed chain would then have active end groups or radicals that react with iron or iron oxide to form iron fluorides. These fluorides constitute Lewis acid sites that are highly aggressive in attacking the PFPE chain itself. The chain thus attacked generates even more Lewis acid sites on the bearing material, cascading the process and thus totally consuming the PFPE[6-9]. Apparently such a catalytically aggressive cascade of events does not occur with a MAC hydrocarbon and that is possibly the reason that the MAC lifetime is longer than that of the PFPEs. As yet, however, no tribochemical mechanism has been proposed to account for the finite lifetime of the MAC.

The recognition that fluoride formation on the bearing surface is a rate-limiting factor in the destruction rate of PFPEs has led to coating the bearing surface with a material that does not allow fast fluoride formation. Titanium carbide (TiC) has been identified as such a material and is now in use as a coating on bearing balls. A study with the SOT has verified that longer 143AC lubricant life can be achieved for TiC-coated balls run on 440C steel plates[10].

Conclusions

The Spiral Orbit Tribometer has been shown here to be capable of evaluating the coefficient of friction and relative degradation rates of liquid lubricants running in the boundary regime in vacuum. Convenient experimental test durations were achieved by restricting the amount of lubricant initially applied to the system to μg quantities, thus allowing the lubricant to be "used up" relatively quickly. Three lubricants were evaluated and found to exhibit coefficients of friction and lifetimes that were experimentally distinguishable from each other. The degradation rate of a multiply alkylated cyclopentane hydrocarbon fluid was almost two orders of magnitude less than the rates for two perfluoropolyalkylethers. The generation of friction polymer and performance of solid lubricant films using this new tribometer will be reported in future papers.

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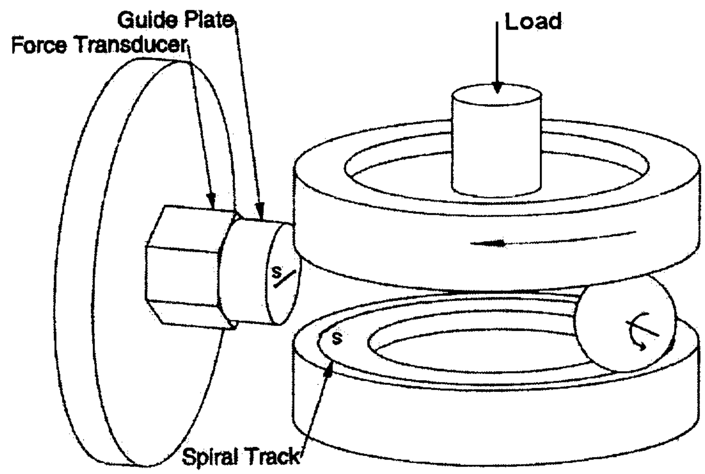

Fig. 1. Elements of the Spiral Orbit Tribometer. S denotes the scrub – the portion of the spiral track made by the ball contacting the guide plate.

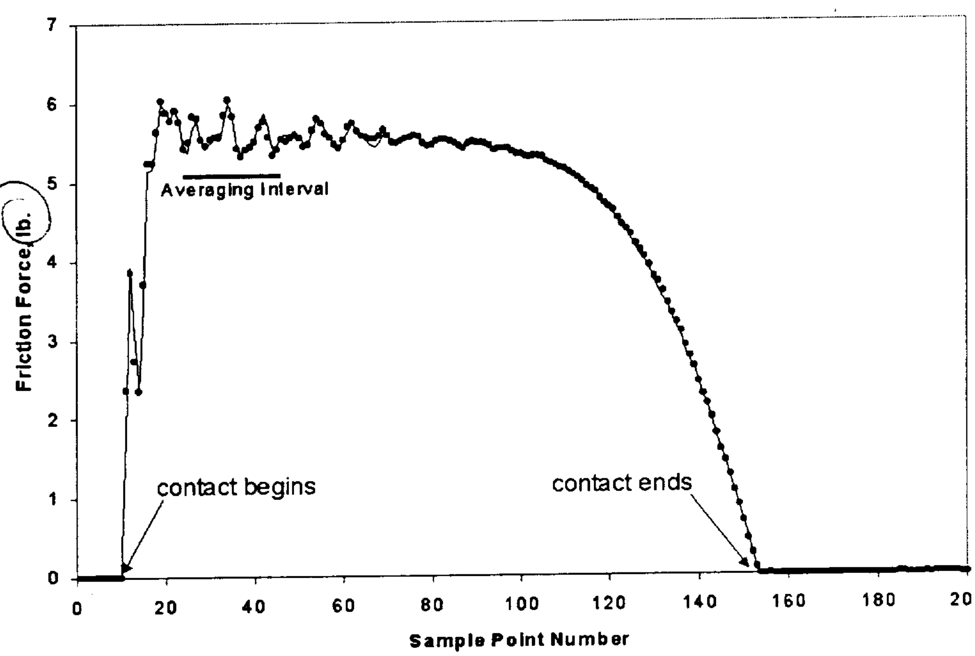

Fig. 2. Typical force profiles for the 56th and 57th orbit of 143AC

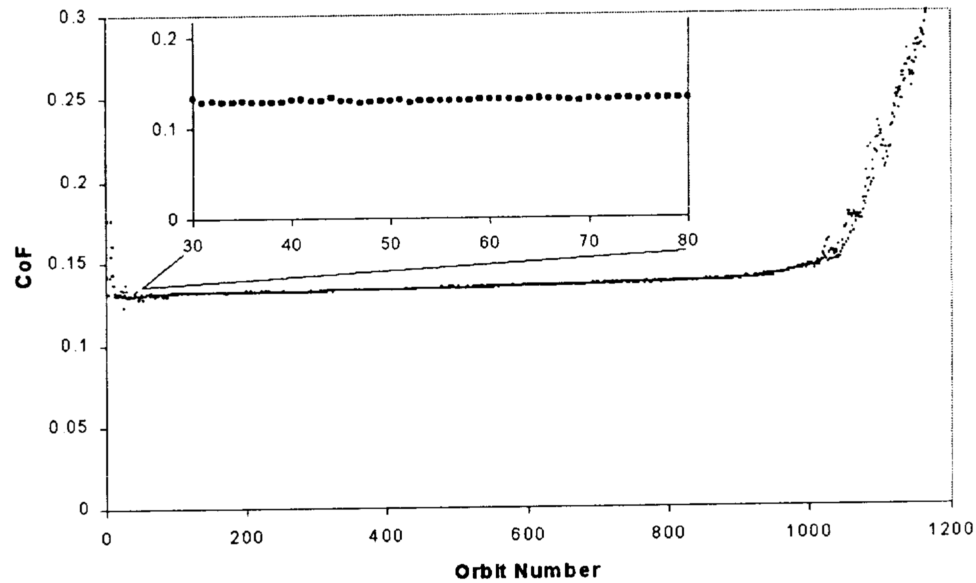

Fig. 3. Friction trace for a test of 143AC. The force profiles in Fig. 2 were from the 56th and 57th orbits of this test.

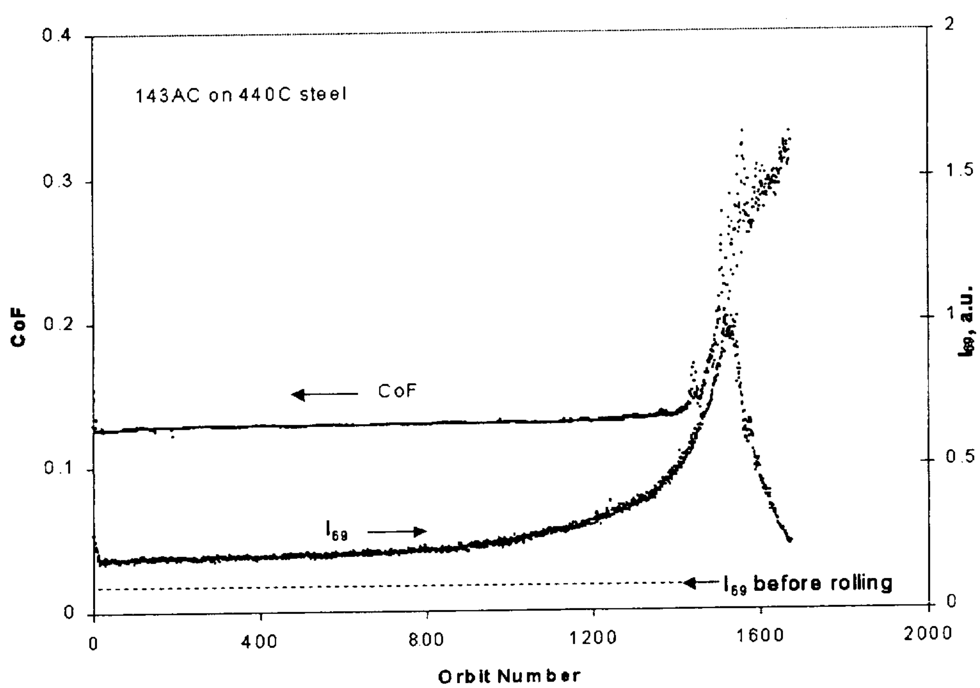

Fig. 4. CoF and intensity of m/e=69, CF_3^+.

Logarithmic bar chart? (12 BARS - 3 GROUPS of 4? - & within each group, in order of CoF?)

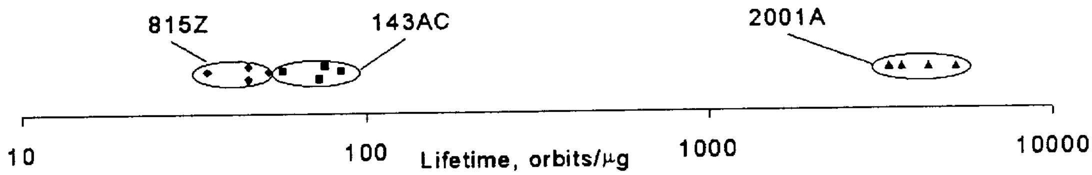

Fig. 5. Normalized lifetimes of the lubricant tests

Lubricant	CoF	Lifetime, Orbits/µg
815Z	.130	34.5
	.121	52.1
	.119	45.4
	.118	45.4
143AC	.132	84.8
	.132	73.2
	.133	57.1
	.136	75.6
2001A	.075	5188
	.078	4313
	.077	3325
	.081	3625

Table 1. Coefficients of friction and normalized lifetimes.